# Point-by-point responses to reviewers

We thank the reviewer for the detailed and thoughtful review of our manuscript entitled "Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China". Those comments are all valuable and very helpful for revising and improving our paper. We think the incorporation of the reviewers' suggestion has led to a much improved manuscript. Detailed below is our response to the issues raised by the reviewers. We also detail the specific changes incorporated in the revised manuscript in response to the reviewers' comments.

## Reviewer #2:

[Comment]: *This paper addresses the severe underprediction of nitrous acid (HONO) concentrations by the Community Multi-scale Air Quality model (CMAQ). However, this underprediction is not very surprising because the model omits gas-phase and many heterogeneous reactions that produce HONO. This paper is a welcome addition to the literature on this important topic although much experimental work to better determine these reactions is needed.*

[Response]:
We appreciate the reviewer's recognition for our work and the valuable comments. We have incorporated the reviewer's suggestion into the revised manuscript. Please check the following point-by-point responses.

[Comment]: *2.1The authors provide a summary of the HONO reactions that they include in their version of the gas-phase Carbon Bond mechanism, CB6r3, in Table 1. Although I am doubtful that much, if any, HONO is produced through gas-phase reaction, NO + NO2 + H2O→2 HONO ($k_f$), the authors should check to see if rate coefficients for this reaction and its reverse, HONO + HONO → NO + NO2 (+ H2O) ($k_r$) are consistent with the HONO equilibrium constant. The equilibrium constant for this pair of reactions is: Keq = ([HONO] [HONO])/([NO][NO2][H2O]) and Keq = kf/kr; this expression is correct regardless, if the system is in equilibrium or not. The value of Keq of 5E-20 derived from Table 1 seems very small considering the value given by Chan et al., (Environ. Sci. Technol., 10, 1976, 674 – 682). [The Chan et al. Keq for HONO was used by Stockwell and Calvert to estimate experimental absorption cross-sections of gas-phase HONO (J. Photochem., 8, 193 - 203, 1978) from equilibrium mixtures. The fact that these HONO absorption cross-sections remain consistent today with those produced by more direct methods (see: Burkholder, et al., "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19," JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019 http://jpldataeval.jpl.nasa.gov) support the validity of the Chan et al. Keq for HONO.]*

[Response]:

The rate coefficients of the gas phase decomposition and formation reactions of HONO in this work are used from the CMAQv5.3-CB6 mechanism without any modification (Yarwood et al., 2010). CB6 chemical mechanism has been widely used to simulate many gas-phase species including HONO (Yarwood and Karamchandani–ENVIRON, 2014). The rate constants in CB6 were obtained from the study of Kaiser and Wu (Kaiser and Wu, 1977) who used a Pyrex surface for their experiment. Chan et al (Chan et al., 1976a; Chan et al., 1976b) used a stainless-steel reactor and reported higher rate constants for these reactions. However, the calculated equilibrium constants in both studies are similar ($5\times10^{-20}$ in CB6 vs. $6\times10^{-20}$ in Chan et al. (1976)).

To clarify this point, we have provided additional discussion in the revised manuscript as follows.

Page 3 Line116-118:

The calculated equilibrium constant in CB6 (Kaiser and Wu, 1977) is similar to reported rate constants by Chan et al ($5\times10^{-20}$ in CB6 vs. $6\times10^{-20}$ in Chan et al. (Chan et al., 1976a; Chan et al., 1976b).

[Comment]: *2.2 The authors make a surprising statement about HONO chemistry at Lines 69 – 70. They state that the reaction, HO + NO -> HONO, was added to WRF-Chem. But this reaction is included in several of the standard chemical mechanisms in the WRF-Chem model. For example, it is included in the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2).*

[Response]:

Thanks to the reviewer for pointing out the inaccurate expression. The research we cited (Li et al, 2010) did not actually modify the reaction, HO+NO →HONO. This reaction was only taken into consideration in their simulation of HONO formation. We have fixed this error by changing the original text in Page 2 Line 70-74 to "Li et al. (2010) examined the impact of HONO chemistry in Mexico City using the Weather Research and Forecasting model, coupled with chemistry (WRF-CHEM). They considered five different HONO reactions: ① the existing homogeneous reaction between NO (nitric oxide) and OH, ② the added heterogeneous reaction of $NO_2$ on the aerosol surfaces, ③ the added heterogeneous reaction of $NO_2$ on the ground surfaces, ④ the added heterogeneous reaction of $NO_2$ with semi-volatile organics, and ⑤ the added $NO_2$ reaction with freshly emitted soot.".

[Comment]: *2.3 Lines 148 – 154: The authors correctly state that several heterogeneous HONO producing reactions have been proposed. The possible significance of heterogeneous chemistry for the production of HONO was proposed several decades ago and it would be good if the authors provides some acknowledgement of that fact. For example, Finlayson-Pitts, B. J., and J. N. Pitts Jr. 2000, "Chemistry of the upper and lower atmosphere: Theory, experiments and applications" New York: Academic Press cite a number of investigations of heterogeneous HONO producing reactions. While I acknowledge that the authors' paper is not a historical review, it would be good if they could provide a clear picture of long search by many international researchers for these heterogeneous reactions.*

[Response]:

The heterogeneous formation reactions of HONO have been proposed several decades ago. Finlayson-Pitts reviewed that the heterogeneous reactions of $NO_2$ occurring at the surfaces of aerosol particles, fogs, buildings, and the ground(Finlayson-Pitts, 2000). Subsequent field and experimental studies have reported that HONO can also form from particulate nitrates (Ye et al., 2016; Bao et al., 2018; Romer et al., 2018). The acid displacement reaction can also form HONO on the surface of nitrous acid (VandenBoer et al., 2013). During past 20 years, many modeling studies involving heterogeneous formation of HONO have been conducted The figure below shows the long research history of HONO heterogeneous reactions carried out by many international researchers.

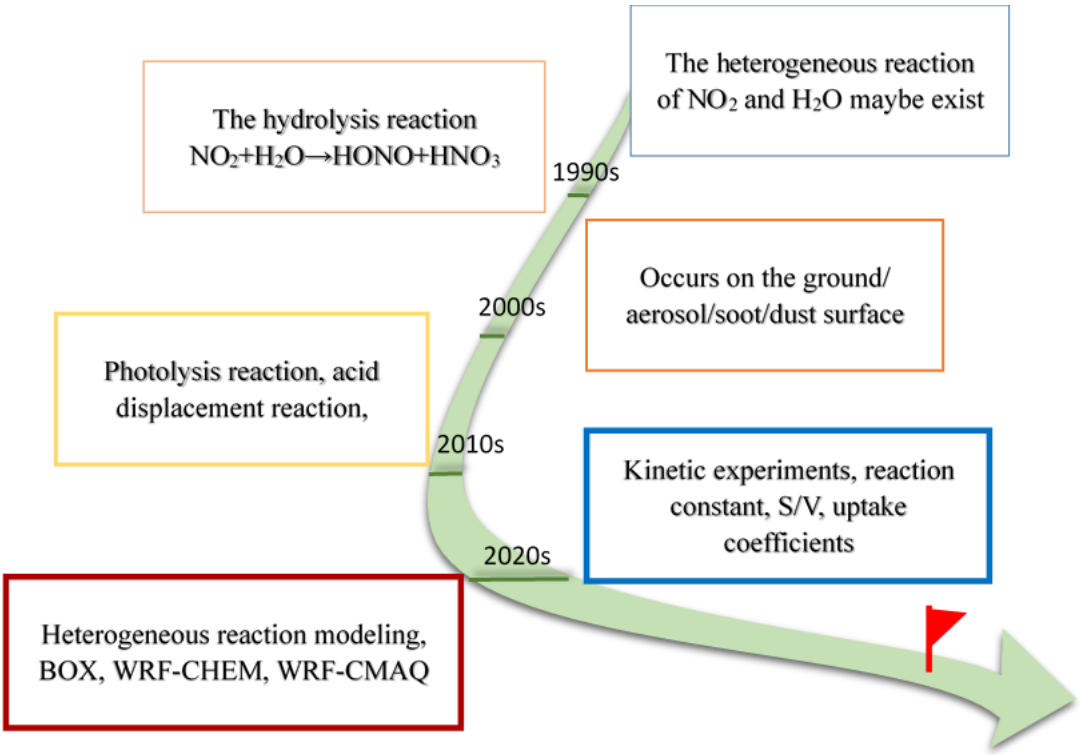


Fig.S1 Research history of heterogeneous reactions of HONO in past decades

As the reviewer suggested, we have added the following discussion in the revised manuscript.

Page 5 Line 152:

The heterogeneous formation of HONO has been studied for several decades. The long research history of HONO heterogeneous reaction can be found in Finlayson-Pitts (Finlayson-Pitts, 2000).

[Comment]: *2.4 In discussing both gas-phase and aqueous-phase photolysis (Lines 120 – 122; 177 – 184; elsewhere?) The authors make a common mistake in terminology. A photolysis rate is the product of a photolysis frequency (or "photolysis rate coefficient" or "J-value") and the concentration of the substance being photolyzed. An example of a photolysis rate is J [HONO]. Absorption cross-section and quantum*

*yield data are used for calculating J but it is not a photolysis rate by itself. Please use either "photolysis frequency" or "photolysis rate coefficient" to describe a J-value to avoid furthering the use of misleading terminology in atmospheric chemistry literature.*

[Response]:

We agree and thank the reviewer to point out our mistake in terminology. We have corrected the term to "photolysis rate coefficient" in the revised manuscript. The corrections are indicated as red.

[Comment]: *2.5 The presented measurements and modeling following Line 266 in the Results and Discussions Section are well performed and very interesting. As expected the authors' modeling found that gas-phase chemistry alone can't explain the observed concentrations. It is striking that the HONO day/night behavior and nighttime concentrations in present-day Beijing are similar to that observed by Platt et al. in Los Angeles during 1980 (Platt et al., Observations of nitrous acid in an urban atmosphere by differential optical absorption, Nature, 285, 312-314, 1980). In summary, the authors have examined the relative importance of the various HONO producing reactions and shown that HONO can have a dominate effect on the HO budget. These results are potentially relevant to the development of policies to improve air quality in large urban regions.*

[Response]:

Thanks for the reviewer's statement about HONO values in present-day Beijing and in Los Angeles during 1980. There are indeed three similar daily characteristics between HONO in Beijing and HONO in Los Angeles during 1980. First of all, from the perspective of concentration, the maximum value of daily HONO concentration in two cities both reached about 2 ppb. Then, HONO has a similar accumulation process at night and a consumption process during the day. Finally, HONO increases the OH concentration through the photochemical reactions during the daytime. When discussing HONO night-time concentration and OH, we referred this influential paper recommended by the reviewer.

Page 9, Line 301：

Consistent with observations at other cities (Platt et al., 1980; Bernard et al., 2015; Fu et al., 2019), the diurnal variation of observed HONO concentrations in Beijing also reveals higher night-time concentrations than day-time values (Fig. 1b).

Page 14, Line 467：

HONO can affect greatly the daily OH budget (Platt et al., 1980; Harris et al., 1982; Li et al., 2018c; Lu et al., 2019; Xue et al., 2020).

[Comment]: *2.6 I strongly suggest that the authors address the gas-phase mechanism points as presented in their paper although I doubt modifications of the rate coefficients for the NO + NO2 + H2O → 2 HONO and HONO + HONO → NO + NO2 (+ H2O) reactions will change their modeling conclusions.*

[Response]:

We thank the reviewer for the suggestion. In this study, we used CB6 gas-phase chemical mechanism without any modification. Chemical kinetics in CB6 are based on the results of Kaiser and Wu (Kaiser and Wu, 1977) which are lower than the values reported by Chan et al. (1976a,1976b). We also performed a separate simulation by using the higher rate constants reported by Chan et al. (1976a, 1976b). As expected, the use of higher rate constants did not change predicted HONO concentrations appreciably which reiterates that the contribution of gas-phase chemistry to HONO concentration is relatively small. The average reaction rate of R2 increase from $4\times10^{-6}$ ppb $h^{-1}$ in HONO_ORI to $4\times10^{-4}$ ppb $h^{-1}$ in HONO_Chan. The average reaction rate of R3 increase from $1.7\times10^{-8}$ ppb $h^{-1}$ in HONO_ORI to $1.7\times10^{-6}$ ppb $h^{-1}$ in HONO_Chan. But the reaction of R2 and R3 has manor effect to the total HONO concentration. It is R1 (NO+OH=HONO) dominate the HONO formation in gas phase.

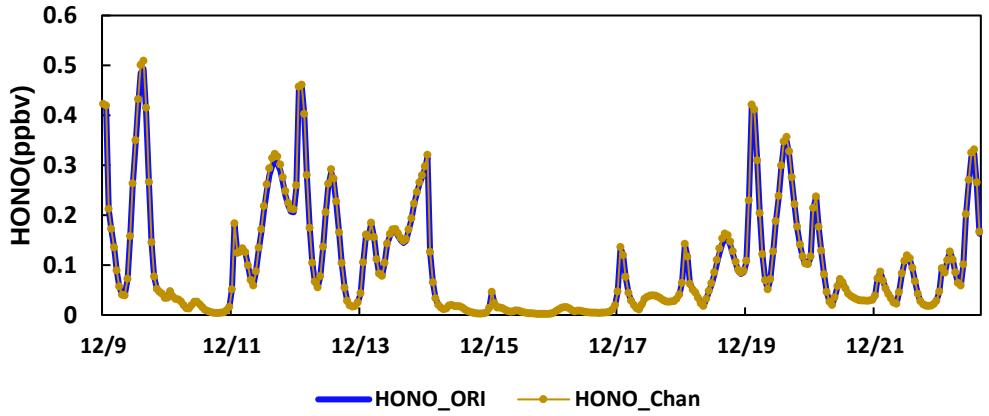


Fig.S5 HONO simulated by default rate coefficients in CB6 (denoted by HONO_ORI) and that measured by Chan et al .(1976) (denoted by HONO_Chan ).

Supplemental Information Page 2, Line 96-102：

Chemical kinetics of R2 and R3 (Table 1) in CB6 are based on the results of Kaiser and Wu (1977) which are lower than the values reported by Chan et al. (Chan et al., 1976a; Chan et al., 1976b). We also performed a separate simulation by using the higher rate constants reported by Chan et al. (1976a, 1976b) (Fig. S4). As expected, the use of higher rate constants did not change predicted HONO concentrations appreciably which reiterates that the contribution of gas-phase chemistry to HONO concentration is relatively small.

**[Reference] :**

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